

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

C564

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification: C03C 1/02, 13/06, C03B 1/02	A1	(11) International Publication Number: <b>WO 95/34514</b> (43) International Publication Date: 21 December 1995 (21.12.95)
(21) International Application Number: PCT/EP95/02906 (22) International Filing Date: 14 June 1995 (14.06.95) (30) Priority Date: 9412007.8 15 June 1994 (15.06.94) GB (71) Applicant (for all designated States except US): ROCKWOOL INTERNATIONAL A/S [DK/DK]; 501 Hovedgaden, DK-2640 Hedehusene (DK). (72) Inventors, and (75) Inventors/Applicants (for US only): SORENSEN, Lars. Møller [DK/DK]; Bismphave 7B, DK-Birkved (DK). CHRISTENSEN, Vagnmund, Rasmussen [DK/DK]; Sønger 11, DK-4000 Roskilde (DK). JENSEN, Søren, Lund [DK/DK]; Rindsgavevej 11, DK-2840 Holte (DK). HOYER, Hans [DK/DK]; Allervejen 22, Ørslev, DK-4000 Roskilde (DK). HEILDGAARD, Thomas [DK/DK]; Kingsovej 44 st.th., DK-2630 Taastrup (DK). (74) Agent: GILL JENNINGS & EVERY; Broadgate House, 7 Eldon Street, London EC2M 7LH (GB).	(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GR, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NQ, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TT, TM, TN, UA, UG, US, UZ, VN. European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LI, MC, NL, PT, SE). OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). ARIPO patent (KE, MW, SD, SZ, UG). Published With international search report.	
(54) Title: PRODUCTION OF MINERAL FIBRES (57) Abstract <p>A mineral charge containing briquettes is melted in a furnace to form a melt from which man-made vitreous fibres are formed. The briquettes are novel and are compression moulded briquettes of particulate inorganic material bonded by a bonding agent which comprises melamines, usually with lime. The briquettes may include vegetable or other fibres to improve green strength.</p>		

WO 95/34514

PCT/EP95/02306

1

### Production of Mineral Fibres

This invention relates to the production of man-made vitreous fibres (MMVF). In particular, it relates to a method comprising forming a melt by melting in a furnace a mineral charge which includes moulded briquettes of particulate inorganic material and forming MMV fibres from the melt. The charge may consist solely of moulded briquettes or it may comprise a mixture of briquettes with other inorganic material. The invention also relates to novel briquettes.

Many methods are known for forming shaped bonded bodies of particulate mineral material. For instance mineral ore can be pelletised by being tumbled with a binder in the presence of moisture, and moulded briquettes can be made by various techniques. A general review of these moulding techniques was given by John D Higginbotham at a meeting in Seattle USA in October 1993 in a paper entitled "Molasses as an Environmentally Acceptable Briquette and Agglomerate Binder". In this paper Dr Higginbotham reviewed the use of, for instance, starch, polyvinyl alcohol, lignin sulphonate, lime, resins and molasses as binders for briquetting a range of inorganic particulate materials.

In particular, he described that molasses had been used as a binder in coal briquettes but gave poor green strength unless performance was improved by an additive, and that the use of molasses with lime resulted in increased green strength but gave weakened briquettes upon subsequent oven curing. He describes the use of phosphoric acid as an additive for improving the performance of molasses but also examined various other additives. He commented that when agglomerating carbon black, lignin begins to decompose at 250°C but that molasses withstood a temperature of 300°C. He also commented that steel fines waste could be agglomerated using a molasses-lime binder but that the resultant lumps can only be used for recycling the fines to the basic oxygen iron ore furnace since the

CONFIRMATION COPY

WO 95/34514

PCT/KP95/02306

2

higher temperatures of about 1100°C in a steel making blast furnace would generate fines. Also, it seems that the molasses lime binder also includes some phosphoric acid.

In US 2,578,110 briquettes of glass batch are moulded from very finely divided inorganic material, water and optionally glucose, bentonite or other material as binder, and are then heated in an oven for 1/2 hour to 3 hours. The resultant briquettes are melted in a tank to provide a glass melt. In US 2,970,924, lignosulphonic acid salts are used as binder in the pelletising of glass batch for the manufacture of fibre glass. Accordingly this does not involve making briquettes by moulding. The intention is that the pellets will melt faster and more evenly and that there will be improved heat transfer through the melted batch. The briquettes and pellets in these two references are added into the melt and do not have to be significantly self-supporting while they are melting.

In conventional furnaces for providing the melt from which MMV fibres are formed, the melt is made by melting in the furnace a self-supporting column of solid coarse mineral material. This solid coarse material can consist of raw crushed rock but often comprises briquettes formed of finer particulate mineral material. It is necessary that the column shall be self-supporting in order to hold the solid material above melt in the base of the furnace. It is therefore necessary that any briquettes which are included in the charge should retain their integrity while being heated up to near the melt temperatures (which exceed 1,000°C). Disintegration of the briquettes at lower temperatures, of only a few hundred °C, is unsatisfactory since the briquettes will disintegrate into powder and the column of coarse material will tend to collapse resulting in increased resistance to the combustion air, increased pressure and pressure variations in the bottom disturbing the flow of melt through the outlet.

It is therefore necessary that the briquettes should be heat resistant in the sense that the briquettes retain

CONFIRMATION COPY

WO 93/34514

PCT/EP93/02306

3

their briquette structure for as long as possible while they are being heated in the furnace up towards the melting temperature. It is also necessary that it should be possible to make the briquettes by a simple process that avoids the long (several days) curing time needed for hydraulic binders. It would be desirable for the briquettes to have a high green strength, that is to say it would be desirable to be able to handle the briquettes very soon after manufacture, without any curing process and without risk of the fresh briquettes disintegrating.

In US 2,976,162, briquettes are formed using a mixture of clay (such as bentonite) and starch. Although these may be intended to give adequate green strength and strength in the furnace (due to the clay) this system appears to be unsatisfactory and has not been widely adopted. Instead, the attainment of adequate heat resistance and strength has conventionally been achieved by bonding the briquettes using a hydraulic binder, generally cement.

The use of hydraulic binder systems gives satisfactory results but suffers from some disadvantages. One disadvantage is that the process is relatively slow in that the wet mix is formed and shaped and then has to be left to cure for several days.

Another disadvantage is that the particulate material needs to be relatively coarse if satisfactory strength is to be obtained using conventional binders such as cement. For instance at least 10% by weight of the particles normally have to be above 2mm or even 5mm, and frequently 30% have to be above 1mm. Satisfactory results are not obtained with hydraulic and other conventional binders when the particle size is uniformly small, for instance below 1mm. Since the composition must melt within the furnace in a predetermined time, the relatively coarse particles must have a composition which will melt rapidly at the furnace temperature and/or must be associated with a fluxing agent. It is difficult to provide economic, relatively coarse, materials or blends that meet all these requirements,

CONFIRMATION COPY

WO 95/34514

PCT/EP93/02306

4

especially when it is desired that the melt should have low alumina content since many low-alumina materials tend to have a very small particle size and a high melting point.

Another disadvantage is that the hydraulic binder contributes to the inorganic elemental analysis of the final melt and the fibres. For instance cement or clay inevitably contributes alumina to the briquettes and this is undesirable when the briquettes are to be used for the manufacture of fibres having low alumina content.

It is known that the solubility of mineral fibres in physiological saline solutions can be increased by appropriate selection of the composition of the melt. As a generality, best results at pH 7.5 are sometimes alleged when the amount of aluminium in the melt, measured as oxides, is below 3 or 4% (preferably not more than 1 or 2% by weight  $Al_2O_3$ ). Accordingly, if biological solubility in saline at pH 7.5 is required the mineral material for forming the briquettes, and any additional material that is included in the charge, has to be selected so that it complies both with the required low aluminium content and with the requirement that the melt has appropriate melt properties. Thus the charge must result in a melt having appropriate melting temperature and viscosity characteristics such that the melt has appropriate fibre-forming properties.

Many minerals that might otherwise be considered to be suitable for the manufacture of low  $Al_2O_3$  MMV fibres have an alumina content that is sufficiently high that even if those minerals alone were used the final analysis of the MMV fibres would have an alumina value that is higher than the 3 or 4% limit that is desired. The fact that, in practice, it is necessary to add also conventional inorganic briquetting binder such as cement or alkali slag or clay places a further restriction on the particulate minerals that can be used.

It would therefore be desirable to provide briquettes which allowed simpler manufacturing procedures than

CONFIRMATION COPY

WO 95/34514

PCT/EP95/02306

5

existing briquetting techniques that utilise hydraulic binders, whilst ensuring that the resultant briquettes do not collapse significantly in the furnace prior to melting. It would also be desirable to provide a briquetting system that could utilise inorganic particulate materials which tend to be unsatisfactory in existing briquetting systems and/or which is particularly suitable for the production of fibres having low alumina content.

According to the invention, MMV fibres are made by a method comprising forming a melt by melting in a furnace a mineral charge which includes compression-moulded briquettes of particulate inorganic material bonded by a bonding agent which comprises molasses, and forming fibres from the melt.

The invention is applicable to the production of any MMV fibres made from a vitreous melt, such as of rock, slag, glass or other mineral melt. The particulate inorganic material from which the briquettes are formed, and the total charge, may thus be formulated so that the fibres have the desired analysis. Generally the mix from which the briquettes are formed includes substantial amounts (measured by weight of inorganic oxides) of  $\text{SiO}_2$  and alkaline earth and/or alkali metal oxides.

The amount of  $\text{SiO}_2$  is generally at least 30% and often at least 35% or 40%. The total amount of alkaline earth and/or alkali metal oxides is usually above 20% and preferably above 30%. It is particularly preferred that the amount of  $\text{CaO} + \text{MgO}$  is in the range 20 to 50% and the amount of  $\text{CaO}$  is often in the range 10 to 35%. The mix may also include polyvalent metal oxides such as  $\text{FeO}$ ,  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  in an amount above 1%. The amount of these polyvalent metal oxides can be as much as, for instance, 35% or 40% but is often below 15% or 20%.

When high solubility at pH 7.5 is required the amount is generally below 10% and preferably below 5% and the  $\text{Al}_2\text{O}_3$  content in the briquettes is preferably below 4%, most preferably below 2%. The combined amount of  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$

CONFIRMATION COPY

WO 95/34514

PCT/EP95/02306

6

is generally not more than 6% and is preferably below 4%. The combined amount of FeO + MgO + CaO is preferably below 50%. The total charge may also be within these ranges. A preferred composition of this type is 45-60% SiO<sub>2</sub>, 0.5-4% Al<sub>2</sub>O<sub>3</sub>, 0.1-4% TiO<sub>2</sub>, 5-12% FeO, 10-25% CaO, 8-18% MgO, 0-4% Na<sub>2</sub>O, 0-2% K<sub>2</sub>O, 0-6% Na<sub>2</sub>O + K<sub>2</sub>O, 2-10% P<sub>2</sub>O<sub>5</sub> and 0-10% others.

The invention can also be usefully applied to the production of MMV fibres having higher Al<sub>2</sub>O<sub>3</sub> content, for instance up to 30%. The novel briquettes may have an analysis within the same ranges.

A preferred composition for the fibres, and optionally for the briquettes, is 32-48% SiO<sub>2</sub>, 10-30% Al<sub>2</sub>O<sub>3</sub>, 10-30% CaO, 2-20% MgO, 2-15% FeO, 0-10% Na<sub>2</sub>O + K<sub>2</sub>O, 0-6% TiO<sub>2</sub>, 0-16% P<sub>2</sub>O<sub>5</sub> + B<sub>2</sub>O<sub>3</sub>, and 0-15% other elements. Usually the amount of Al<sub>2</sub>O<sub>3</sub> is above 18% but it can be lower, in which even the amount of P<sub>2</sub>O<sub>5</sub> + B<sub>2</sub>O<sub>3</sub> is usually at least 1%. Preferably SiO<sub>2</sub> is 34-45%, Al<sub>2</sub>O<sub>3</sub> is 19-28%, CaO is 14-25% and MgO is 5-15%. SiO<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub> is often 60-75%, preferably 61-63%. The composition is preferably such that it has a viscosity at 1,400°C of 10 to 70 poise and a dissolution rate of at least 20mm per day when measured at a pH of 4.5.

The briquettes used in the invention can substantially retain their strength in the furnace until melting occurs even though the melt temperature is usually at least 1100° and often at least 1200°C. Accordingly, the charge of briquettes and optionally other solid coarse material can be provided as a self-supporting column which extends above melt in the base of the furnace and the briquettes can retain their integrity while being heated up to above the melt temperatures. Instead of collapsing to generate fines within the column of solid charge, thus significantly reducing the permeability of the charge and tending to collapse the charge, the briquettes start to collapse only at about the temperature at which significant melting starts to occur. Thus the charge does not collapse in the column above the melting region but instead retains its

CONFIRMATION COPY

WO 95/34514

PCT/EP95/02306

7

coarse open particulate nature until it has sunk down into the melting region in the furnace and has melted.

For instance, when the strength of various briquettes is measured under increasing temperatures, it is found that the briquettes in the invention can start to undergo significant deterioration in strength only at temperatures above 1000°C, for instance at or above 1100°C, which is about the same range as the range at which briquettes bonded with conventional hydraulic binders start to lose significant strength.

It is very surprising that the use of a combustible organic material, namely molasses, can contribute to a binder system that substantially retains its strength to temperatures above 1000 or about 1100°C. It seems that there may be some interaction between the molasses and the mixture of elements which is necessarily present in the particulate inorganic material which is included in the moist mix which is subjected to compression moulding.

The bonding agent comprises molasses, by which we mean molasses alone or reaction products of molasses with additives. It may also include a secondary binder which can be inorganic or organic. For instance the molasses binder can be used in combination with a secondary organic binder such as starch, synthetic resin such as phenol-formaldehyde, or lignin (preferably calcium lignosulphonate). The molasses (including additives that react with the molasses) preferably provides at least 30% and usually at least 60% (dry weight) of the total binder system in the briquettes.

The molasses binder can include an activator which provides a borate or a phosphate, preferably phosphoric acid but alternatively a phosphate such as a sodium or calcium phosphate. Preferably, however, the molasses binder includes lime as activator, and preferably the binder is substantially free of added phosphate or phosphoric acid or borate. However in some instances it

CONFIRMATION COPY



WO9534514

PCT/KP9502306

8

can be desirable to include phosphate, when it is desired for the fibres to include phosphorous.

Preferably the binder consists of molasses and lime with no other added activator. The lime can be added as  
5 calcium oxide or calcium hydroxide, for instance as burnt lime, quick lime or hydrated lime.

The amount of lime is preferably 50 to 150% of the stoichiometric amount required for reaction between sugars in the molasses and calcium to form a sugar-calcium  
10 complex. Thus the amount of lime, measured as CaO, is generally at least 0.1 parts per part by weight molasses and is usually at least 0.5 parts. Generally there is no necessity for it to be more than about 0.7 parts but it can be as much as 0.9 or even 1.2 parts.

The molasses can be any conventional molasses. The content is usually around 40-55% sugars, 5-15% minerals, 20-30% water, 5-20% other organics. It is generally unnecessary, but if desired the molasses can have a higher water content, in which event the amount of molasses that  
15 is used may be increased proportionately above the amounts quoted below. The total amount of molasses is usually in the range 1 to 15%, often around 2 or 3 to 8%, most preferably about 5% based on the total weight of the mix.

The amount of lime, measured as CaO, is usually in the  
20 range 1 to 10%, often 2 to 5% based on the total weight of the mix.

The total amount of free moisture in the mix at the time of compression moulding is usually in the range 0.5 to 10%, preferably around 1 to 5%, most preferably 1 to 3%,  
30 based on the total weight of the mix. Some of this moisture is provided by the molasses but the remainder may be provided associated with the particulate inorganic material or may be added as a deliberate addition of moisture.

The briquettes are normally made by mixing the  
35 particulate inorganic material (and optionally vegetable fibres) with the molasses (and lime), allowing the

CONFIRMATION COPY

WO 9534514

PCT/EP95/02306

9

resultant mix to stiffen and then moulding the mix. If a supplementary binder is being used, it is generally included as a mixture with the molasses or may be included in the mix before or after adding the molasses. The stiffening of the mix and of the binder results in the product becoming substantially uniformly tacky and more viscous and resistant to mixing, prior to moulding. The preparation of the mix for moulding is accelerated if the mix has an elevated temperature, and suitable heat rise can be provided by applying mechanical energy or heat energy to the mix or by exothermic reaction, for instance between the lime and water and/or molasses.

When the particulate inorganic material all has a desired fine particle size, the formation of the mix may be achieved merely by mixing the particulate material with the binding system, generally at a temperature in the range 20 to 70°C. However when some or all of the particulate material is too coarse, it is preferably crushed prior to or during the mixing of the molasses and this crushing generates heat energy which will cause the desired increase in temperature. For instance the particulate material may be simultaneously mixed, crushed and heated by use of a rod mill.

The molasses can be added and mixed into the mix in the rod mill but it is generally more convenient to form the mix of particulate material (and optionally vegetable fibres) by crushing and mixing in a rod mill and then to add the molasses in a subsequent mixing stage, for instance in a traditional paddle mixer or cement mixer.

The lime can be incorporated into the mix before or after adding the molasses. For instance the lime can be included during the rod milling or other crushing stage or can be added after crushing and prior to adding molasses or can be added after adding molasses. If convenient, it can be added simultaneously with the molasses.

In a preferred process the total mix (excluding lime and molasses) is crushed in a rod mill, thereby generating

WO 95/34514

PCT/EP95/02306

10

a temperature rise, the mix is then transferred to a conventional mixer such as a cement mixer or other paddle mixer, the molasses is added with mixing to give a substantially homogeneous mix and then the lime is added.

5 The incorporation of the lime generally results in an exothermic reaction, for instance between calcium oxide and water. This can be utilised for reducing the free moisture content of the mix before or after adding molasses and, in particular, it can be utilised to increase the temperature  
10 of the mix to promote stiffening before moulding. For instance the use of 45 to 82% burnt lime (based on the amount of molasses) can easily cause a temperature rise to around 60°C.

The mix is maintained at an appropriate elevated  
15 temperature to allow stiffening due to reaction between molasses and lime to progress, and this may be conducted either in the initial mixer or in a pre-feeder where it is held for a few minutes (eg 1/2 to 5 or 10 minutes) before transfer to the moulding apparatus.

20 The moulding can be by any suitable compression technique. However it is strongly preferred that the moulding should be by means of a roller press. A roller press mould comprises a pair of rolls that rotate together to define a nip, with mould recesses in at least one of the  
25 rolls or, usually, with matching mould recesses in both of the rolls. The rolls can have a substantial axis length or may be wheels. Roller briquetting presses of this general type are well known for the purpose of palletising animal feedstuffs or for making fuel briquettes,

30 The pressure applied on the mix in the mould is often in the range of 10 to 50 kN per line cm.

The dimensions of the recesses dictate the dimensions of the briquettes that are obtained. Generally each  
35 briquette has a minimum dimension of at least 5mm and usually at least 40mm. The maximum dimension can be up to, for instance, 200mm but is usually not more than 150mm. A typical size is 100mm by 50mm.

CONFIRMATION COPY

WO 93/34514

PCT/EP95/02306

11

The briquettes can be discharged from the press within a few minutes of the mix being charged into the press or pre-feeder. At this stage the briquettes made in the invention have adequate green strength to allow reasonable handling immediately upon removal from the moulds. It is not necessary to heat them in an oven to achieve adequate strength. Preferably they are then allowed to stand (usually exposed to the atmosphere) for a short while, for instance  $\frac{1}{2}$  to 2 hours, generally about  $\frac{1}{2}$  hour or up to an hour, by which time they have acquired additional strength. The briquettes can then be handled in conventional manner. Accordingly the briquettes do not require prolonged storage (as is required with conventional binders) to allow hydraulic bonding to occur but can, instead, be handled and used almost immediately after moulding.

The briquettes can be formed from particulate inorganic materials which are conventional for forming MMVF-forming briquettes although the materials can be finer than conventional and can, if desired, provide a low alumina content.

When using a hydraulic binder, it is necessary to include a significant amount of coarse material in the mix in order that the briquette has adequate strength. In the invention, however, this is not required and so the particulate material substantially can consist of material having a particle size smaller than is conventional for MMVF briquettes. Thus, although it is possible to perform the invention usefully with particulate material having size at least 90% below 2mm, preferably the size of the particulate material is less than this. For instance usually at least 98% (by weight), and preferably 100%, by weight is below 2mm. In particular, preferably at least 80%, for instance 50-80%, is below 1mm and most preferably below 0.5mm. The presence of some coarser material, eg at least 20% above 1mm, can be desirable. The particulate material is often mainly above 0.1mm and usually mainly above 0.2mm.

CONFIRMATION COPY

WQ93/34514

PCT/EP9502306

12

The use of the relatively fine particle size has two significant advantages. First, it allows, under equal residence time and temperature conditions in the furnace, more rapid melting than is permissible with conventional coarser particle size materials and it allows the use of higher melting point materials. For instance at least 70% by weight of the components of the inorganic material may be materials with a melting point above 1450°C. Second, it allows the use of low  $Al_2O_3$  or other materials that are readily available in a fine particulate form, notably sand.

Thus, if desired, in the invention the entire particulate material in the briquettes can be sand. The fine particle size also minimises or eliminates the need to incorporate fluxing agents, and thus avoids the constraints they provide on the choice of chemical composition.

Suitable fines that can be used include stone fines (such as slag fines conventionally generated in the preparation of minerals for mineral melt production), glass waste, iron ore, used foundry sand, and various MMV waste fibrous materials, for instance that are waste from the fibre-forming process or are unused or waste final product. Prior to the invention it has often not been possible to use MMV waste in significant amounts. Such fibrous materials include spinner waste from the spinning process and the spinning chamber, dry wool waste that is waste cured fibre products such as waste parts of slabs, rolls, pipe sections and so forth, wet wool waste which is uncured wool due to stops in the manufacturing process and other discontinuities in production, and filter mats.

Instead of or in addition to the inclusion of inorganic fibres, it is desirable to include organic fibre in the mix from which the briquettes are formed. Preferred organic fibres are vegetable (including wood) fibres, especially paper fibres seaweed fibres, citrous waste and straw. The use of straw is advantageous in that it can be introduced dry, and thus does not influence the moisture content of the mix from which the briquettes are formed

CONFIRMATION COPY

WO9524514

PCT/KP95/01306

13

whereas the other fibres may be introduced most conveniently in wet form, in which even their introduction into the mix will influence the moisture content of the mix. The use of the vegetable fibres can result in improved green strength in the briquettes and can result in satisfactory or improved green strength being attained over an increased range of moisture contents. The amount of vegetable or other organic fibres is generally from 0.2 to 10 parts, often around 0.5 to 5 parts, per part by weight molasses. The straw is usually cut or chopped to a length not more than about 5 or 10mm and this is a suitable maximum for all vegetable fibres.

The particulate mineral material for forming the briquettes may be crushed mineral material or naturally occurring fine particulate mineral material. Suitable materials are high temperature melting components such as quartz, olivine sand, limestone, dolomite, rutile, bauxite, iron ore, magnesite, magnetite, and brucite. Other conventional components for MMVF briquettes such as slag, rock and mineral products like diabase and basalt can be used.

The mineral materials selected for forming the briquettes will be chosen having regard to the chemical analysis and melting properties that are required. Generally below 75%, and often below 20% by weight of the briquette is molten at 1250°C but usually the briquette is totally melted at 1300°C and often at 1375°C.

The mineral charge in the furnace may consist solely of the molasses bonded briquettes or some (for instance up to 70% by weight, usually not more than 50% by weight) of the mineral charge may be introduced in some other form. For instance some of the charge may include briquettes bonded in some other manner, for instance using cement, or may include conventional components for forming MMV fibre melts, such as rock, slag, glass waste and other conventional materials. If the remainder of the charge is not introduced as briquettes, it is normally introduced in

CONFIRMATION COPY

WO95/34514

PCT/EP95/02306

14

a form having a particle size generally in the range 40mm to 160mm. When low alumina content is required in the final fibres, the supplementary materials will generally have a content of alumina of not more than 6% by weight, preferably below 4% and will preferably be such that the total charge has an alumina content of below 4%, preferably below 2%. When high alumina content is required, the total charge will be selected so as to yield the desired composition.

10 The molasses-bonded briquettes or the remainder of the charge may include components that are known to be useful to promote solubility such as phosphorous and boron compounds generally in a total amount of not more than 10 to 20% (measured as oxides).

15 The furnace may be any furnace in which the melt is provided by melting a self supporting column of solid coarse mineral material comprising the briquettes. This column is often at least 1 metre high. The furnace may be an electrical furnace or a tank furnace or, preferably, it is a cupola furnace in which combustible material is included in the charge. The melt temperature will depend upon the minerals being used and the fibre-forming technique but is generally in the range 1200 to 1600°C, often around 1400 to 1550°C.

25 Fibre formation can be by conventional techniques such as a spinning cup technique or, preferably, by pouring on to a spinner comprising at least two co-operating spinning wheels, for instance as described in WO92/06047. Thus the fibres may be made by pouring the melt on to a first spinning rotor from which the melt is thrown in sequence on to one or more subsequent spinning rotors off which the fibres are thrown.

30 The products of the invention can be used for any of the conventional uses of MMV fibres, such as thermal insulation, noise reduction and regulation, fire protection, growth media, reinforcement and fillers.

CONFIRMATION COPY

WO 95/34514

PCT/EP95/02306

15

The invention includes also the novel briquettes and the methods of making them. In particular, the invention includes compression-moulded briquettes formed from inorganic material providing (measured by weight of oxides) above 30%  $\text{SiO}_2$ , above 20% alkaline earth and/or alkali metal oxides and which optionally contain vegetable fibres and which contain a molasses binder.

In each of the following examples the mineral material and the organic and inorganic waste is crushed and mixed in a rod mill. Due to the released energy from the crushing, there is a temperature rise in the rod mill. The mixture is transferred into a traditional cement mixer and the molasses is added while mixing. Within about two minutes the mixture is homogeneous and burnt lime is then added. This generates an exothermic reaction and the mixture acquires a temperature of about 60°C. The mixture is then transferred to a pre-feeder and held in that for a few minutes before being transferred into the moulding cavities of a roller press in which the mix is pressed at a pressure above 20 kN per line cm into briquettes which typically have a size of 100mm by 50mm. The briquettes are discharged from this press within a few minutes of the initial mixture being charged into the prefeeder and the moulds. Upon discharge, the briquettes have a smooth shiny surface and appear to have a high density. They have a green strength such that they substantially all withstand a 2 metre drop test immediately after discharge from the moulds.

They are allowed to stand for about  $\frac{1}{2}$  hour. Either immediately, or after any convenient storage period, the briquettes are charged into a cupola furnace that is also charged with coke as a fuel and optionally with other coarse inorganic material. Pre-heated air is injected into the furnace near its base and the heating and combustion of coke caused by this initiates the melting process at the base of the column of briquettes and other charge. The process is continued with material supply such that the

CONFIRMATION COPY



W09534514

PCT/EP95021306

16

melt temperature is around 1,510°C. The melt runs from the furnace to the upper spinning rotor of a spinner broadly as described in W092/06047. The resultant MNV fibres are collected as a mat and may be bonded using organic binder in a conventional manner.

In all the experiments in the invention the column of briquettes maintains a permeable structure and there is substantially no collapse of the briquettes significantly before melting. This is in contrast to what happens when thermally unstable briquettes are used in that they tend to degrade during the pre-heating, when they have a temperature of only a few hundred °C and this causes the column to be dense and relatively impermeable. This leads to an increase in pressure inside the furnace resulting in pulses of melt flowing from the outlet of the furnace. In the experiments of the invention the melt flows uniformly from the furnace outlet, indicating that the column is permeable and that a constant pressure exists within the furnace.

#### 20 Example 1

The charge is formed of 45% diabase, 7% dolomite and 48% briquettes. The briquettes have an inorganic content of 23% bauxite, 19% converter slag, 35% waste from mineral wool production, 20% fly ash and 3% burnt lime, and 5% molasses (based on the total weight of the mix) is used as binder. The moisture content of the mix at the time of compression moulding is 9%. The fibre composition is

	SiO <sub>2</sub>	38.7%
	Al <sub>2</sub> O <sub>3</sub>	22.0%
30	TiO <sub>2</sub>	1.9%
	FeO	6.8%
	CaO	16.9%
	MgO	9.1%
	Na <sub>2</sub> O	1.9%
35	MnO	0.3%
	P <sub>2</sub> O <sub>5</sub>	0.3%

#### Example 2

CONFIRMATION COPY

WO 95/34514

PCT/EP95/02306

17

The charge is formed of 45% by weight of type A briquette and 55% by weight type B briquette. Type A briquettes are made from 39% quartz sand, 16% olivine sand, 28% converter slag, 14% iron ore and 3% burnt lime, together with 5% molasses based on the total weight of the mix. These briquettes have an estimated melting temperature of about 1264°C.

The type B briquettes are formed from 36% quartz sand, 35% olivine sand, 15% apatite, 9% mineral wool production waste and 3% burnt lime, together with 5% molasses. These briquettes have a melt temperature of about 1363°C.

The analysis of the fibres is

	SiO <sub>2</sub>	53.9%
	Al <sub>2</sub> O <sub>3</sub>	1.8%
15	TiO <sub>2</sub>	0.5%
	FeO	6.8%
	CaO	16.7%
	MgO	14.7%
	Na <sub>2</sub> O	0.2%
20	K <sub>2</sub> O	0.4%
	MnO	0.4%
	P <sub>2</sub> O <sub>5</sub>	3.6%

#### Example 2

The charge is formed of 45% type C briquettes and 55% type D briquettes. The type C briquettes are formed from 6% lemon waste, 14% iron ore, 3% burnt lime, 26% converter slag, 35% quartz sand and 16% olivine sand. The briquettes are bonded with 5% (based on the remainder of the mix) molasses.

The type D briquettes are formed of 15% apatite, 36% quartz sand, 37% olivine sand, 9% mineral wool production waste and 3% burnt lime, together with 5% molasses.

The resultant fibres have the composition

	SiO <sub>2</sub>	53.2%
35	Al <sub>2</sub> O <sub>3</sub>	1.9%
	TiO <sub>2</sub>	0.5%
	FeO	7.6%

CONFIRMATION COPY

WO 95/34514

PCT/EP95A02306

18

	CaO	15.5%
	MgO	15.5%
	Na <sub>2</sub> O	0.2%
	K <sub>2</sub> O	0.4%
5	MnO	0.4%
	P <sub>2</sub> O <sub>5</sub>	3.8%

In the following examples, the properties of the briquettes are determined 60 minutes after starting mixing. All moisture contents are determined at the time of addition of the lime.

#### Example 4

Briquettes are formed from 3 parts (by weight) quartz sand, 15 parts olivine sand, 3 parts bauxite, 73 parts mineral wool production waste, 6 parts apatite, 4 parts hydrated lime and 3 parts molasses together with various additives and added moisture to give specified free moisture contents at the time of compression moulding.

When no extra additive is included, the briquettes have a strength of about 4.5 kN when the moisture is about 2% and about 3 kN when the moisture is about 5%.

When 9 parts lemon pectin waste is included the briquettes have a strength of about 10 kN at 2% moisture or at 4% moisture and about 6 kN at 7% moisture.

When 11 parts seaweed pectin is included the product has a strength of about 22 kN at 1% moisture and 13 kN at 5% moisture.

When predried wet paper waste is included the strength is significantly increased to values between 6 and 11 kN over a range of moisture contents from 2 to 5%.

These results show that the fibrous additives result in an increase in green strength and in reduced sensitivity to the amount of free moisture in the mix.

When the strength of the briquettes is measured as the briquettes are subjected to increased temperature, it is found that the briquettes made without any additives undergo a small and insignificant loss of strength at about 825°C but only undergo significant loss of strength at

CONFIRMATION COPY

WO 95/34514

PCT/KP95/02306

19

temperatures between 1122 and 1167°C. When the same test is performed using briquettes made with the pectin or paper additives, generally similar results are obtained.

#### Example 5

- 5 Briquettes are formed from 6 parts quartz sand, 30 parts olivine sand, 6 parts bauxite, 46 parts waste from mineral wool production, and 12 parts apatite, with 4 parts lime and 3 parts molasses.

- 10 When 4 parts cut straw is included in the mix the strength is 9 kN at 2.5% moisture content and 6.5 kN at about 4% moisture content when using cut straw having a length of about 5mm, and rather less than this when using ground straw. Without the straw, the strength is 4.5 kN at 2% moisture and 2 kN at 4% moisture.

#### Example 6

- 15 Briquettes are made from 10 parts (by weight) quartz sand, 50 parts olivine sand, 10 parts bauxite, 10 parts waste from mineral wool production and 20 parts apatite, together with 10 parts molasses.

- 20 In one set of experiments, briquettes are made with 4% hydrated lime and, optionally, with 2% pregelatinised starch. The strength after 60 minutes from the start of mixing is about 0.5 to 1.5 kN higher, at constant moisture content, when starch is present than when it is omitted.

- 25 In another series of experiments the mix is formed at 4.75% moisture content with either 4% hydrated lime or 4% cement. The strength is determined one hour after mixing and at various intervals up to 50 hours. The mix formed with lime has an initial strength in this test of about 3  
30 kN after 1 hour and it increases to about 8 kN after 48 hours, while the mix made using cement has an initial strength after 1 hour of about 0.5 kN and it increases after 48 hours to 4.2 kN. Thus the inclusion of the lime is giving strength far greater than is attainable using  
35 cement. It can be concluded that the lime must be interacting with the molasses rather than acting as a hydraulic binder.

CONFIRMATION COPY

WO 95/34514

PCT/EP93/02306

20

**CLAIMS**

1. A method of making MMV fibres comprising forming a melt by melting in a furnace a mineral charge and forming fibres from the melt, characterised in that the mineral charge includes compression-moulded briquettes of particulate inorganic material bonded by a bonding agent which comprises molasses.
2. A method according to claim 1 in which the briquettes have been made by compression moulding at 10 to 50 kN/line cm.
3. A method according to any preceding claim in which the briquettes have been made by roller moulding.
4. A method according to any preceding claim in which the briquettes have been made by mixing the particulate inorganic material with the molasses binder in the presence of moisture, allowing the binder to start to stiffen and then moulding the stiffened mixture under pressure.
5. A method according to any preceding claim in which the furnace is a cupola furnace.
6. A method according to any preceding claim in which the MMV fibres are made by pouring the melt on to a first spinning rotor from which the melt is thrown in sequence on to one or more subsequent spinning rotors off which the fibres are thrown.
7. A method according to any preceding claim in which the briquettes include fibres.
8. A method according to any preceding claim in which the charge, the fibres and the briquettes have a content (measured by weight as oxides) of below 4t  $Al_2O_3$ .
9. A method according to claim 8 in which at least 50t by weight of the charge is provided by compression-moulded briquettes formed by compression moulding a particulate mineral material having a size at least 90t below 2mm with a binder that is substantially free of alumina and that comprises molasses.
10. A method according to any preceding claim in which the fibres have a content, measured by weight of oxides, of 45-

CONFIRMATION COPY

WO 9534514

PCT/EP95/02306

21

60%  $\text{SiO}_2$ , 0.5-4%  $\text{Al}_2\text{O}_3$ , 0.1-4%  $\text{TiO}_2$ , 5-12%  $\text{FeO}$ , 10-25%  $\text{CaO}$ , 8-18%  $\text{MgO}$ , 0-4%  $\text{Na}_2\text{O}$ , 0-2%  $\text{K}_2\text{O}$ , 0-6%  $\text{Na}_2\text{O} + \text{K}_2\text{O}$ , 2-10%  $\text{P}_2\text{O}_5$  and 0-10% others.

11. A method according to any of claims 1 to 7 in which the fibres contain, measured by weight of oxides, 32-48%  $\text{SiO}_2$ , 10-30%  $\text{Al}_2\text{O}_3$ , 10-30%  $\text{CaO}$ , 2-20%  $\text{MgO}$ , 2-15%  $\text{FeO}$ , 0-10%  $\text{Na}_2\text{O} + \text{K}_2\text{O}$ , 0-6%  $\text{TiO}_2$ , 0-16%  $\text{P}_2\text{O}_5 + \text{B}_2\text{O}_3$  and 0-15% other elements.

12. A method according to any preceding claim in which the briquettes include vegetable fibres.

13. A method according to any preceding claim in which the bonding agent comprises molasses and lime.

14. A method according to claim 13 in which the amount of lime, measured as  $\text{CaO}$ , is 0.1 to 1 (preferably 0.2 to 0.7) parts by weight per part by weight molasses.

15. A method according to claim 12 or claim 13 in which the briquettes have been made by a method comprising adding lime as  $\text{CaO}$  to a moist mix of the particulate inorganic material, thereby causing an increase in the temperature of the mix, and adding molasses to the mix before, while or after adding the lime.

16. A method according to any preceding claim in which the briquettes substantially retain their strength in the furnace until they melt, the melt temperature in the furnace is at least  $1100^\circ\text{C}$ , and the mix from which the briquettes are formed includes substantially amounts (measured by weight of oxides) of  $\text{SiO}_2$  (preferably above 30%) and alkaline earth and/or alkali metal oxides (preferably 20 to 50%  $\text{CaO} + \text{MgO}$ ).

17. Briquettes which are bonded, compression-moulded, briquettes of particulate inorganic material comprising (measured by weight of oxides) above 30%  $\text{SiO}_2$  and at least 20% alkaline earth and/or alkali metal oxides (preferably 20 to 50%  $\text{CaO} + \text{MgO}$ ), and in which the briquettes are bonded by molasses preferably in combination with lime.

18. Briquettes according to claim 17 including vegetable fibres.

CONFIRMATION COPY